Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

of the manuscript:

Shape persistent macrocycle with a self complementary recognition pattern based on diacetylene linked alternating hexylbenzene- and perfluorobenzene- rings

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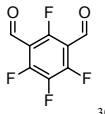
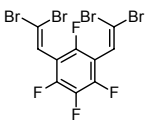
Synthetic protocols and analytical data

General: All reagents were purchased from Aldrich or ABCR and were used without further purification. Dry solvents were obtained by standard literature procedures, in particular THF and toluene by distillation from a Na/benzophenone slurry and CH2Cl2 was distilled over CaH. All reactions were carried out under N2 protection gas atmosphere. 1H-NMR and 13C-NMR spectra were recorded on a Bruker Ultra Shield 300 MHz and 500 MHz, the J values are given in Hz. MALDI-TOF MS spectra were recorded on a PerSeptive Biosystems Voyager –DE PRO time-of-flight mass spectrometer. EI-MS were recorded on a Finnigan MAT 95Q mass spectrometer. Thin layer chromatography (TLC) was carried out on Merck silica gel 60 F254 plates and column chromatography (CC) using Merck silica gel 60 (0.040-0.063 mm). Elemental analyses were recorded using a ThermoQuest FlashEA 1112 N/Protein Analyzer.



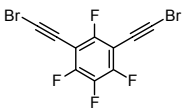
2

Tetrafluoroisophthalaldehyde (**2**) was synthesized according to a reported protocol.[1]:
To 2,3,4,6-Tetrafluoroisophthalonitrile (10.89 g, 54.43 mMol) in argon bubbled toluene (500 mL) at 0°C a 1.5 M diisopropylaluminiumhydride toluene solution (100 mL, 150 mMol) was added. After 2.5 h at room temperature the reaction mixture was cooled to 0°C. EtOAc (20 mL) and 2N HCl (300 mL) was added. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic layers were adsorbed on silica (30 g). Column chromatography (silica, toluene) yielded in **2** (5.34 g, 25.91 mMol, 48 %) as beige solid. ^{1}H-NMR($CDCl_3$): 10.15 (*s*, 2H). ^{13}C-NMR($CDCl_3$): 111.77 (*m*); 137.42 (*d,t,d* J_d = 255, J_t = 15, J_d = 6); 154.29 (*d,m* J_d = 255); 159.71 (*d,m* J_d = 255); 181.48 (*d* J = 6). EI-MS: 207 (9); 206 (100, M^+); 205 (61); 177 (55); 149 (57); 99 (35).



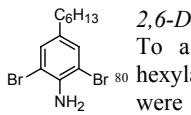
3

1,3-Bis-(2',2'-dibromoethenyl)-2,4,5,6-tetra-fluorobenzene (**3**):
To a suspension of CBr_4 (50 g, 150 mMol) and zinc powder (9.75 g, 150 mMol) in dry CH_2Cl_2 (100 mL), a solution of PPh_3 (39.5 g, 150 mMol) in dry CH_2Cl_2 (400 mL) was added dropwise over 2 h at RT. After completed addition, the mixture was stirred for 20 h. A solution of **2** (7.5 g, 36 mMol) in dry CH_2Cl_2 (80 mL) was added to the above suspension. After stirring for 2 h, the suspension was filtered through a silica short plug with CH_2Cl_2. Further purification by CC (silica, hexane) provided **3** (17.1 g, 33.03 mMol, 92%) as a white solid. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.22 (*s*, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 99.8, 111.6 (*m*), 124.0, 137.8 (*d,m* J_d = 244.2), 148.1 (*d,m* J_d = 255.2), 150.7 (*d,m* J_d = 251.3). EI-MS *m/z* 517.4 [M^+]. Anal. calcd. for $C_{10}H_2Br_4F_4$ (517.7): C 23.20, H 0.39; found: C 23.29, H 0.62.



4

1,3-Bis-bromoethynyl-2,4,5,6-tetrafluoro-benzene (**4**):
To a solution of **3** (11.0 g, 21 mMol) and benzyltriethylammoniumchloride (0.5 g, 2.2 mMol) in THF (100 mL), a solution of KOH (60 g, 1.07 mol) in water (60 mL) was added. The mixture was stirred for 2 h at RT. The organic phase was separated and washed with saturated aqueous $NaHCO_3$. Purification by CC (silica, hexane) afforded **4** (7.0 g, 19.7 mMol, 94%) as a white solid. ^{13}C-NMR (75 MHz, $CDCl_3$) δ 62.9 (*q* J = 3.5 Hz), 65.1 (*d* J = 3.75 Hz), 100.0 (*t,m* J_t = 22.2), 137.5 (*d,m* J_d = 252.0), 152.6 (*d,m* J_d = 259.9), 160.0 (*d,m* J_d = 257.7). EI-MS *m/z* 355.9 [M^+]. Anal. calcd. for $C_{10}Br_2F_4$ (355.9): C 33.75; found: C 33.59.



5

2,6-Dibromo-4-hexyl-phenylamine (**5**):
To a 1000 mL flask in an ice/water bath 4-hexylanniline (25 g, 141 mMol) and DMF (200 mL) were added. A solution of N-bromosuccinimide (62.5 g, 0.35 mol) in DMF (200 mL) was added dropwise within 1 hour to the stirred hexylaniline solution. The reaction mixture was stirred for another 3 h. After removing of DMF with reduced pressure, purification by CC (silica, hexane) afforded **5** (40 g, 119 mMol, 85%) as a red crystal. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.92 (*t*, 3H), 1.31 (*br*, 6H), 1.55 (*m*, 2H), 2.48 (*t*, 2H), 4.42 (*s*, 2H), 7.22 (*s*, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.6, 23.0, 29.2, 31.8, 32.1, 34.8, 109.2,

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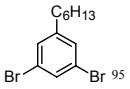
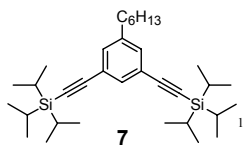
131.9, 135.0, 140.1. EI-MS *m/z* 334.8 [M^+]. Anal. calcd. for $C_{12}H_{17}Br_2N$ (335.08): C 43.01, H 5.11; found: C 43.33, H 4.88.



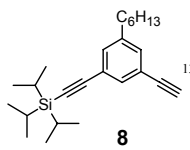
6

1,3-Dibromo-5-hexyl-benzene (**6**):
A 1000 mL flask equipped with a magnetic stirrer, a reflux condenser and an oil bath was charged with **5** (40 g, 119 mMol) in dry ethanol (800 mL) and concentrated H_2SO_4 (50 mL). The reaction mixture was stirred and heated to 75°C and $NaNO_2$ (25 g, 362 mMol) was added in small portions. After completed addition, the reaction mixture was stirred for another 2 h at 75°C. Subsequently the reaction mixture was cooled in an ice bath and ice-water (300 mL) was added. Extraction with CH_2Cl_2, drying over $MgSO_4$ and evaporation of the solvents provided the crude product. CC (silica, hexane) yielded **6** (26 g, 81.2 mMol, 68%) as colorless oil. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.92 (*t*, 3H), 1.30 (*s*, 6H), 1.60 (*m*, 2H), 2.56 (*t*, 2H), 7.28 (*d*, 2H), 7.50 (*t*, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.6, 23.0, 29.3, 31.5, 32.1, 35.8, 123.2, 130.7, 131.7, 147.2. EI-MS *m/z* 319.8 [M^+]. Anal. calcd. for $C_{12}H_{16}Br_2$ (320.06): C 45.03, H 5.04; found: C 45.33, H 5.11.



7

1-Hexyl-3,5-bis-[2',2'-(triisopropyl-silanyl)-ethynyl]-benzene (**7**):
To a 500 mL flask equipped with a reflux condenser **6** (8 g, 25 mMol), triisopropylacetylene (15.5 g, 85 mMol), dry triethylamine (150 mL), $Pd(PPh_3)_4$ (0.8 g, 0.67 mMol) and CuI (0.26 g, 1.3 mMol) were added. The suspension was degassed with N_2 and stirred for 18 h at 80°C under a N_2 atmosphere. After removal of the solvent, CC (silica, hexane) provided **7** (11.2 g, 21.4 mMol, 86%) as a colorless oil. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.92 (*t*, 3H), 1.16 (*s*, 42H), 1.32 (*br*, 6H), 1.60 (*m*,2H), 2.60 (*t*, 2H), 7.25 (*d*, 2H), 7.41 (*t*, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 11.7, 14.5, 19.0, 23.0, 29.3, 31.6, 32.0, 35.8, 91.0, 106.8, 123.9, 132.4, 133.0, 143.4. EI-MS *m/z* 522.2 [M^+-H]. Anal. calcd. for $C_{34}H_{58}Si_2$ (523.00): C 78.08, H 11.18; found: C 77.84, H 10.97.



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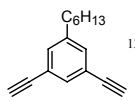
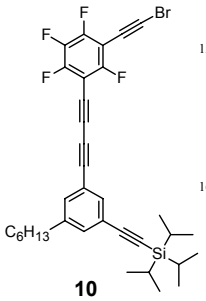


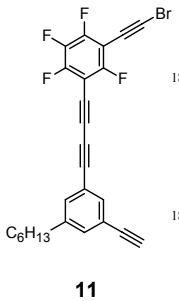
9

3-Ethynyl-5-hexyl-phenylethynyl)-triiso-propylsilane (**8**) and *1,3-diethynyl-5-hexyl-benzene* (**9**):
TBAF (0.15 g) in THF (15 ml) was dropped to the stirred solution of **7** (15 g, 28.7 mMol) in wet THF (150 mL) (containing 1% water) over 30 minutes. After stirring for 4 h at RT, removal of the solvent followed by CC (silica, hexane) provided **8** (2.9 g, 7.9 mMol, 28%) and **9** (1.09 g, 5.2 mMol,18%) both as colorless oils. The remained starting compound **7** was recovered. *3-Ethynyl-5-hexyl-phenylethynyl)-triisopropyl-silane* (**8**): ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.93 (*t*, 3H), 1.16 (*s*, 21H), 1.32 (*br*, 8H), 1.63 (*m*, 2H), 2.60 (*t*, 2H), 3.08 (*s*, 1H), 7.30 (*m*, 2H), 7.47 (*t*, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 11.7, 14.5, 19.1, 23.1, 29.3, 31.5, 32.1, 35.9, 77.6, 83.5, 91.3, 106.8, 122.5, 124.1, 132.4, 132.7, 133.4, 143.6; EI-MS *m/z* 366.1 [M^+]. Anal. calcd. for $C_{25}H_{38}Si$ (366.6): C 81.89, H 10.45; found: C 81.90, H 10.21; *1,3-diethynyl-5-hexyl-benzene* (**9**): ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.91 (*t*, 3H), 1.32 (*br*, 6H), 1.58 (*m*, 2H), 2.58 (*t*, 2H), 3.08 (*s*, 1H), 7.31 (*s*, 2H), 7.47 (*t*, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.5, 23.1, 29.2, 31.5, 32.0, 35.9, 77.8, 83.3, 122.6, 132.9, 133.4, 143.6; EI-MS *m/z* 210.1 [M^+]. Anal. calcd. for $C_{16}H_{18}$ (210.3): C 91.37, H 8.63; found: C 91.11, H 8.48.



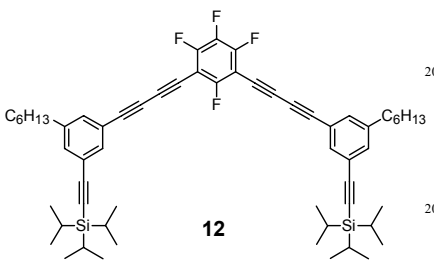
10

1-(2',3',4',6'-tetrafluoro-5'-bromo-ethynylphenyl)-4-(3''-hexyl-5''-triiso-propylsilaneethynylphenyl)-buta-1,3-diyne (**10**):
A 250 mL flask was charged with **4** (3.56 g, 10 mMol), $Pd_2(dba)_3$·$CHCl_3$ (0.103 g, 0.1 mMol) and CuI (0.05 g, 0.26 mMol) in dry toluene (120 mL) and dry diisopropylethylamine (12 mL). The solution was degassed by bubbling with N_2. A solution of **8** (0.80 g, 2.2 mMol) in dry toluene was added dropwise within 2 h at RT. The reaction mixture was stirred for another 2 h at RT. Removal of the solvents under reduced pressure and CC (silica, hexane) afforded **10** (0.90 g, 1.4 mMol, 64%) as a yellow solid. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.90 (*t*, 3H), 1.14 (*s*, 21H), 1.32 (*br*, 6H), 1.61 (*m*,2H), 2.58 (*t*, 2H), 7.32 (*t*, 2H), 7.50 (*t*, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 11.2, 14.1, 18.6, 22.6, 28.9, 31.0, 31.6, 35.4, 62.6, 64.8, 65.1, 73.0, 84.2, 84.6 (*q*), 91.6, 99.5 (*t,m* J_t = 32.6), 105.8, 120.8, 124.0, 132.3, 133.4, 133.5, 137.3 (*d,m* J_d = 251.1), 143.6, 152.7 (*d,m* J_d = 260.6), 160.3 (*d,m* J_d = 258.6). MALDI-ToF-MS *m/z* 641.3 [M+H]$^+$ calcd. for $C_{35}H_{37}BrF_4Si$ (640.18).



11

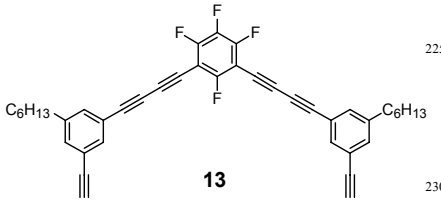
1-(2',3',4',6'-tetrafluoro-5'-bromoethynyl-phenyl)-4-(3''-hexyl-5''-ethynylphenyl)-buta-1,3-diyne (**11**):
A solution of TBAF (0.4 g, 1.53 mMol) in THF (15 ml) (pH = 7.5, adjusted with AcOH) was added dropwise to a solution of **10** (0.7 g, 1.1 mmol) in wet THF (50 mL) (containing 1% water) over 30 minutes. The reaction mixture was stirred for e h at RT before the solvents were removed under reduced pressure. CC (silica, hexane) gave **11** (0.03 g, 0.06 mMol, 5.6%) as colorless oil. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.90 (*t*, 3H), 1.32 (*br*, 6H), 1.63 (*m*,2H), 2.59 (*t*, 2H), 3.10 (*s*, 1H), 7.35 (*s*, 2H), 7.49 (*t*, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.1, 22.5, 28.8, 31.0, 31.6, 35.4, 62.7, 64.8, 65.3, 73.0, 77.9, 82.5, 83.9, 84.5, 99.7, 121.0, 122.6,132.9, 133.4, 133.6, 137.3 (*d,m* J_d = 253.3), 143.7, 152.4 (*d,m* J_d = 259.4), 160.0 (*d,m* J_d = 256.4). MALDI-ToF-MS *m/z* 484.3 [M]$^+$ calcd. for $C_{26}H_{17}BrF_4$ (484.0).



12

1,3-di-(4'-(3''-hexyl-5''-triisopropylsilane-ethynylphenyl)-buta-1',3'-diynyl)-2,4,5,6-tetra-fluorobenzene (**12**):
A 500 mL flask was charged with **4** (3.0 g, 8.4 mMol), $Pd_2(dba)_3$·$CHCl_3$ (0.20 g, 0.19 mMol) and CuI (0.26 g, 1.36 mMol) in dry toluene (150 mL) and dry diisopropylethylamine (15 mL). The solution was degassed by bubbling with N_2. A solution of **8** (6.2 g, 16.9 mMol) in dry toluene was added dropwise and the reaction mixture was stirred for 3 h at RT under N_2. Removal of the solvents under reduced pressure and CC (silica, hexane) provided **12** (5.2 g, 5.6 mMol, 67%) as a light brown solid. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.93 (*t*, 6H), 1.16 (*s*, 42H), 1.32 (*br*, 12H), 1.63 (*m*,4H), 2.60 (*t*, 4H), 7.34 (*t*, 4H), 7.52 (*t*, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 11.3, 14.1, 18.6, 22.6, 28.9, 31.0, 31.6, 35.4, 65.1, 73.0, 84.3, 84.7 (*d*),

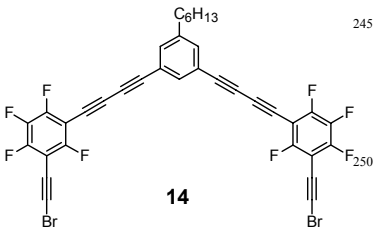
91.6, 99.5 (*t,m* J_t = 21.9), 105.8, 120.8, 124.0, 132.3, 133.4, 133.5, 137.3 (*d,m* J_d = 247.6), 143.6, 152.6 (*d,m* J_d = 261.1), 160.3 (*d,m* J_d = 261.2). EI-MS *m/z* 926.0 $[M-H]^+$. Anal. calcd. for $C_{60}H_{74}F_4Si_2$ (927.39): C 77.71, H 8.04; found: C 77.46, H 7.70.



13

1,3-di-(4'-(3''-hexyl-5''-ethynyl-phenyl)buta-1',3'-diynyl)-2,4,5,6-tetrafluorobenzene (**13**):

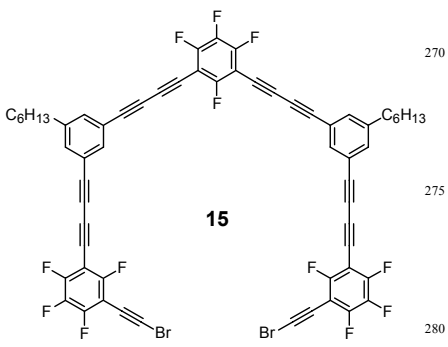
TBAF (0.5 g) in THF (50 mL) was added dropwise to the stirred solution of **12** (2.0 g, 2.2 mMol) in wet THF (150 mL) (containing 1% water) over 30 minutes. After stirring for 4 h at RT, the solvents were removed under reduced pressure and CC (silica, hexane) of the residue gave **13** (1.05 g, 1,7 mMol, 79%) as brown solid. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.91 (*t*, 6H), 1.33 (*br*, 12H), 1.61 (*m*,4H), 2.60 (*t*, 4H), 3.10 (*s*, 2H), 7.36 (*t*, 4H), 7.50 (*t*, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.5, 23.0, 29.2, 31.4, 32.0, 35.8, 65.6(*d*), 73.5, 78.3, 82.8, 84.4, 85.0, 99.5 (*t,m* J_t = 22.1), 121.4, 123.0, 133.3, 133.8, 134.0, 137.8 (*d,m* J_d = 252.1), 144.1, 152.6 (*d,m* J_d = 261.9), 160.2 (*d,m* J_d = 261.1). EI-MS *m/z* 614.0 $[M^+]$. Anal. calcd. for $C_{42}H_{34}F_4$ (614.71): C 82.06, H 5.57; found: C 81.86, H 5.69.



14

1,3-di-(4'-(2'',3'',4'',6''-tetrafluoro-5''-bromo-ethynylphenyl)buta-1',3'-diynyl)-5-hexylbenzene (**14**):

A 100 mL flask was charged with **4** (1.0 g, 2.8 mMol), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.02 g, 0.019 mMol) and CuI (0.02 g, 0.1 mMol) in dry toluene (20 mL) and dry diisopropylethylamine (1 mL). The solution was degassed by bubbling with N_2. A solution of **9** (0.07 g, 0.33 mMol) in dry toluene (2 mL) was added dropwise and the reaction mixture was stirred for 3 h at RT under N_2. Removal of the solvents under reduced pressure and CC (silica, hexane) afforded **14** (0.09 g, 0.12 mMol, 36%) as a brown solid. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.91 (*t*, 3H), 1.32 (*br*, 6H), 1.62 (*m*, 2H), 2.61 (*t*, 2H), 7.41 (*d*, 2H), 7,54 (*t*, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.0, 22.6, 28.8, 30.9, 31.6, 35.4, 62.8 (*q,* d_q = 3.3), 64.7 (*t,* J_t = 3.1), 65.6 (*t,* J_t = 3.3), 73.5, 83.4, 84.3 (*m*), 99.2 (*t,m* J_t = 18.9), 99.8 (*t,m* J_t = 18.0), 121.4, 133.7, 133.9, 137.3 (*d,m* J_d = 251.8), 144.1, 152.3 (*d,m* J_d = 260.9), 160.0 (*d,m* J_d = 259.6). MALDI-ToF-MS *m/z* 759.5 $[M+H]^+$ calcd. for $C_{36}H_{16}Br_2F_8$ (757.95).



15

1,3-di-(4'-(3''-hexyl-5''-(4'''-(2'''',3'''',4'''',6'''-tetrafluoro-5''''-bromo-ethynyl-phenyl)buta-1''',3'''-diynyl)-phenyl)buta-1',3'-diynyl)-2,4,5,6-tetrafluorobenzene (**15**):

A 100 mL flask was charged with **4** (0.8 g, 2.2 mMol), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.02 g, 0.019 mMol) and CuI (0.02 g, 0.1 mMol) in dry toluene (20 mL) and dry diisopropylethylamine (1 mL). The solution was degassed by bubbling with N_2. A solution of **13** (0.2 g, 0.33 mMol) in dry toluene (2 mL) was added dropwise and the reaction mixture was stirred for 3 h at RT under N_2. Removal of the solvents under reduced pressure and CC (silica, hexane) afforded **15** (0.2 g, 0.17 mMol, 53%) as a brown solid. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.92 (*t*, 6H), 1.32 (*br*, 12H), 1.65 (*m*, 4H), 2.62 (*t*, 4H), 7.42 (*s*, 4H), 7.55 (*d*, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.0, 22.6, 29.0, 31.0, 31.6, 35.4, 62.8, 64.7, 65.6, 73.5, 83.4, 83.6, 84.3 (*m*), 84.5 (*m*), 99.2 (*m*), 99.5 (*m*), 100.0 (*m*),121.4, 133.7, 134.0, 137.3 (*d,m* J_d = 250.6) 137.5 (*d,m* J_d = 252.0), 144.1, 152.3 (*d,m* J_d = 260.4), 152.7 (*d,m* J_d = 261.9) 160.0 (*d,m* J_d = 259.6), 160.3 (*d,m* J_d = 259.7). APCI-MS *m/z* 1164.0 $[M^+]$. Anal. calcd. for $C_{62}H_{32}Br_2F_{12}$ (1164.7): C 63.94, H 2.77; found: C 64.32, H 2.90.

7,8,9,25,26,27,43,44,45,56,58,60-Dodecafluoro-17,35,53-trihexyl-heptacyclo [41.3.1. 1 6,10. 1 15,19. 1 24,28. 1 33,37. 1 42,46]hexatriaconta-1(55), 6, 8, 10(56), 15, 17, 19(57), 24, 26, 28(58), 33, 35, 37(59), 42, 44, 46(60), 51, 53-octadecaene-2, 4, 11, 13, 20, 22, 29, 31, 38, 40, 47, 49-dodecayne (**1**):

Macrocycle **1** *from* **15** *and* **9**:

A stirred solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.04 g, 0.04 mMol) and CuI (0.02 g, 0.1 mMol) in dry toluene (450 mL) and dry diisopropylethylamine (5 mL) was degassed by bubbling with N_2. Within 10 h a solution of **15** (0.140 g, 0.12 mMol) and **9** (0.025 g, 0.12 mMol) in dry toluene (400 mL) was added dropwise under a N_2 atmosphere. After stirring for 4 days the solvents were removed under reduced pressure. The residue was dissolved in toluene (15 mL), filtered and purified by size exclusion chromatography (SEC, Bio-Beads® S-X1, toluene) to provide **1** (9.6 mg, $7.9{\cdot}10^{-6}$ Mol, 6.6%) as brown solid. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.91 (*t*, 9H), 1.28 (*br*, 24H), 2.21 (*br*, 6H), 6.67 (*br*, 6H), 7.08 (*br*, 3H). ^{13}C-NMR (125 MHz, d_8-Toluene, 50 °C) δ 13.8, 22.5, 29.1, 30.4, 31.6, 34.9, 66.1, 74.6, 81.4, 84.5, 100.0 (*m*), 121.9, 132.3, 134.1, 136.5 (*d,m* J_d = 255), 143.6, 152.0 (*d,m* J_d = 255), 160.5 (*d,* J_d = 255). APCI-MS *m/z* 1212.2 $[M^+-H]$. Anal. calcd. for $C_{78}H_{48}F_{12}$ (1213.2): C 77.22, H 3.99; found: C 76.95, H 4.12.

Macrocycle **1** *from* **13** *and* **14**:

A stirred solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.03 g, 0.03 mMol) and CuI (0.015 g, 0.078 mMol) in dry toluene (700 mL) and dry diisopropylethylamine (3 mL) was degassed by bubbling with N_2. Within 10 h a solution of **13** (61.4 mg, 0.10 mMol) and **14** (75 mg, 0.10 mMol) in dry toluene (120 mL) was added dropwise under a N_2 atmosphere. After stirring for 4 days the solvents were removed under reduced pressure. The residue was dissolved in toluene (15 mL), filtered and purified by SEC (Bio-Beads® S-X1, toluene) and CC (silica, toluene) to provide **1** (5.1 mg, $4.2{\cdot}10^{-6}$ Mol, 4.2%) as brown solid.

Macrocycle **1** *from* **4** *and* **9**:

A stirred solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.21 g, 0.2 mMol) and CuI (0.1 g, 0.5 mMol) in dry toluene (1300 mL) and dry diisopropylethylamine (5 mL) was degassed by bubbling with N_2. Within 10 h a solution of **4** (0.712 g, 2 mMol) and **9** (0.42 g, 2 mMol) in dry toluene (500 mL) was added dropwise under a N_2 atmosphere. After stirring for 4 days the solvents were removed under reduced pressure. The residue was dissolved in toluene (15 mL), filtered and purified by size exclusion chromatography (SEC, Bio-Beads® S-X1, toluene) and CC (silica, toluene) to provide **1** (1.2 mg, $1{\cdot}10^{-6}$ Mol, 0.15%) as brown solid.

Concentration- and temperature dependent ^{1}H-NMR investigations

Table. Chemical shifts of the exo-annular and the endo-annular protons of the macrocycle **1** at different concentrations and temperatures. Chemical shifts for the monomer (δ_m) and the dimer (δ_d) as well as the dimerization constants (K_2) at different temperatures were obtained by fitting the data to the equation[2] below using the Origin® software from Microcal™.

$$\delta = \delta_m + (\delta_d - \delta_m)\,[1+\{(1-(8\cdot K_2\cdot \mathrm{Conc} + 1)^{1/2}/(4\cdot K_2\cdot \mathrm{Conc})\}]$$

Temp (°C)	40		30		20		10		0	
Conc.[a]	H_{endo}	H_{exo}	H_{endo}	H_{exo}	H_{endo}	H_{exo}	H_{endo}	H_{exo}	H_{endo}	H_{exo}
11,062	7,208	6,815	7,149	6,741	7,099	6,681	7,057	6,631	7,023	6,594
10,257	7,215	6,829	7,156	6,753	7,106	6,69	7,06	6,636	7,024	6,596
9,4681	7,221	6,837	7,163	6,761	7,108	6,693	7,064	6,64	7,028	6,598
8,7936	7,226	6,845	7,169	6,77	7,112	6,699	7,069	6,646	7,03	6,602
7,8944	7,241	6,853	7,178	6,782	7,119	6,708	7,073	6,651	7,032	6,605
6,8039	7,259	6,878	7,191	6,8	7,129	6,72	7,083	6,662	7,04	6,612
6,0767	7,273	6,902	7,207	6,817	7,139	6,733	7,087	6,669	7,046	6,618
4,9521	7,301	6,932	7,225	6,843	7,153	6,751	7,101	6,687	7,055	6,628
4,163	7,32	6,963	7,244	6,869	7,169	6,772	7,11	6,703	7,062	6,643
3,6155	7,341	6,984	7,264	6,893	7,181	6,789	7,121	6,713	7,069	6,65
2,9563	7,367	7,037	7,285	6,925	7,203	6,817	7,14	6,735	7,082	6,67
2,3963	7,403	7,092	7,319	6,97	7,225	6,847	7,153	6,755	7,097	6,686
1,8382	7,445	7,143	7,363	7,029	7,256	6,89	7,181	6,788	7,118	6,711
1,342	7,498	7,22	7,405	7,094	7,3	6,948	7,211	6,832	7,14	6,735
0,9125	7,535	7,266	7,463	7,172	7,342	7,007	7,254	6,877	7,173	6,783
0,6232	7,572	7,327	7,514	7,242	7,398	7,081	7,302	6,95	7,217	6,833
δ_m[b]	7,744 ±0,020	7,600 ±0,046	7,835 ±0,031	7,737 ±0,054	7,849 ±0,053	7,762 ±0,089	7,896 ±0,065	7,829 ±0,156	8,072 ±0,211	7,856 ±0,320
δ_d[c]	6,918 ±0,030	6,435 ±0,071	6,948 ±0,054	6,479 ±0,098	6,964 ±0,10	6,506 ±0,171	6,961 0,127	6,51 ±0,308	6,952 ±0,419	6,504 ±0,630
K_2[d]	251 ±35,3	303 ±64	692 ±92	829 ±130	1695 ±309	2054 ±426	3813 ±697	4881 ±1480	11050 ±4908	10268 ±5767
$K_{Dim.}$[e]	277 ±90		760 ±199		1875 ±605		4346 ±2014		10655 ±6158	

[a)]Total concentration of the macrocycle **1** (in mM). [b)]calculated chemical shift for the protons of the monomer. [c)]calculated chemical shift of the protons of the dimer. [d)]calculated dimerization constant (in M^{-1}). [e)]Average association constant of both protons at given temperature (in M^{-1}).

van't Hoff plot of the temperature dependent K_{Dim} values obtained from the ^{1}H-NMR analysis

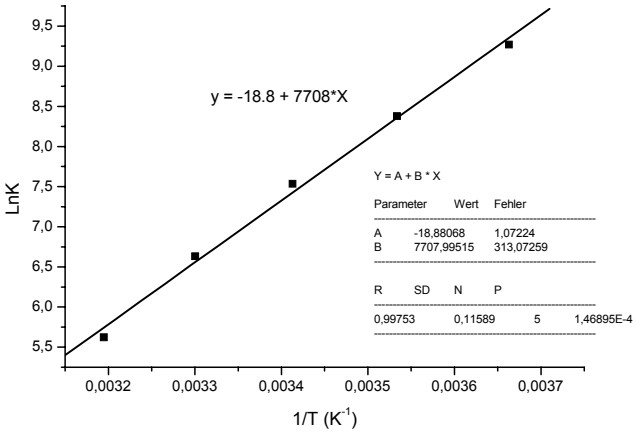


Fig. van't Hoff plot of the dimerization of the macrocycle **1** in $CDCl_3$.

The slope B is equal to -ΔH/R and the axis intercept A is equal to ΔS/R.

With R = 8.314 $Jmol^{-1}K^{-1}$:

$\Delta H = - B \times R = 7708 \times 8.314/1000 = - 64.08 \pm 2.6$ kJ · mol^{-1}

$\Delta S = A \times R = -18.8 \times 8.314 = -156.3 \pm 8.90$ $J \cdot mol^{-1} \cdot K^{-1}$

And at 20°C:

$\Delta G_{293\ K} = \Delta H - T\Delta S$
$= - 64.08 - 293\ (-156.3)/1000 = -18.3 \pm 5.2$ $kJ \cdot mol^{-1}$

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